Thermal Decomposition of Tobacco I. Thermogravimetric Analysis[1]

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Introduction

Preliminary investigation of chemical additives that modify the burning of tobacco indicated a need for studying the controlled thermal decomposition of both treated and untreated tobacco. For this purpose thermogravimetric analysis has been employed. Initially a study was made of untreated tobacco to obtain data which could be used to provide a basis for evaluating the effect of these chemical additives. Four tobacco types and two blends of these tobaccos have been investigated.

Although considerable data have been reported on the thermogravimetric analysis of natural products, comparatively little information appears in the literature on the thermogravimetric analysis of tobacco. In one report weight losses of different tobacco types were discussed in terms of their aroma and combustion (8). In this study ground samples were used, and the thermogravimetric analyses were carried out in static air. In a more recent paper Edmonds *et al.* (2) studied the thermolysis of ground samples of unaged, aged and heat-treated tobaccos in both dynamic air and nitrogen. From the results they were able to characterize the three tobaccos. In another study Kato *et al* (6) investigated the stems from three Japanese tobaccos and discussed the relationship between certain stem constituents and the thermograms.

In the foregoing investigations ground tobacco was used, and different operating conditions were employed. To determine the effect of these operating conditions on the thermal decomposition of tobacco this present study included an investigation of some of these parameters. The conditions studied were: (1) oxidative vs. inert atmosphere, (2) slow vs. rapid heating rate, (3) ground and packed vs. shredded tobacco.

Experimental

An Aminco Thermograv No. 4-4430 was used for the thermogravimetric analyses[3]. Both shredded and ground samples of flue-cured, burley, Maryland and Turkish tobaccos, and two blends of these tobaccos were investigated. The blends consisted of 40% flue-cured, 35% burley, 5% Maryland and 20% Turkish; and 60% flue-cured, 35% burley and 5% Maryland tobaccos. The shredded tobacco and tobacco for the ground samples were taken from unfiltered, 85 mm long cigarettes manufactured on commercial machines. Approximately 95% of the ground samples passed a 35-mesh screen. Prior to analysis all samples were equilibrated at 60% relative humidity and 25°C. Sample sizes ranged from 122 to 125 mg. Thermal decompositions were determined in Coors #000 porcelain crucibles in both air and helium having flow rates of 200 ml per minute. Heating rates of 3 and 15°C per minute were used.

Results and Discussion

The thermogravimetric analysis consisted of heating a known weight of tobacco at a temperature which was increased at a linear rate and recording the change of weight as a function of the temperature. Because of the nature of tobacco and complexity of its thermal decomposition, it was difficult to compare the thermogravimetric curves of the different tobacco types. In many cases small rates of change in weight, which are perhaps indicative of a particular tobacco, were not observed from the thermogram. However, by converting the thermogram to its derivative curve the decomposition pattern was more clearly defined (1, 2, 3, 7). This was done by determining the weight loss in milligrams per degree (dw/dt) for each 10-degree increment over the entire temperature range (25 to 900°C).

Plotting dw/dt versus temperature gave the derivative curve. The advantages of the derivative curve in determining small rates of change in weight can be readily realized by comparing it with the primary thermogram. In obtaining the curve all values for dw/dt were adjusted on the basis of a 100 mg sample. This permitted a better qualitative and semi-quantitative comparison of the curves. It should be noted that the maximum difference between all samples used was less than 3 mg. Large differences in sample size could have sufficiently altered the mode of thermal decomposition of the tobacco to give derivative curves which would not have been useful for comparative purposes.

Because of the non-uniformity of shredded cigarette tobacco, dw/dt cannot be used as an absolute unit for comparative purposes. However, presentation of the thermogravimetric data in the manner described permits a better qualitative and semi-quantitative comparison of the modes of decomposition of various tobacco types and treated tobaccos.

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[3] *Mention of a specific commercial product does not constitute endorsement by the U.S. Department of Agriculture or by the Kentucky Agricultural Experiment Station.*

Each of the observed maxima may be due to loss of one or more leaf components. Such data may help to elucidate many of the complex processes involved in the combustion and pyrolysis of tobacco. They have also been used to provide a basis for evaluating the effect of "chemical modifiers" on the thermal decomposition of tobacco.

Thermal Decomposition in Air-Heating Rate 15°C Per Minute

The thermogravimetric curves (TGA) and derivative thermogravimetric (DTG) curves for the shredded tobacco samples were divided into five zones in which there were characteristic dw/dt maxima (**Figures 1, 2**). The zones were: Zone I (25-150°C), Zone II (150-210°C), Zone III (210-350°C), Zone IV (350-550C°) and Zone V (550-800°C). To compare the course of thermal decomposition for the different types and blends of tobaccos each zone will be discussed separately.

Zone I (25-150°C). The maximum dw/dt in this zone occurred between 60 and 80°C and has been attributed to the volatilization of adsorbed water and low boiling constituents (2). To assess the effect of water on the percent weight loss and dw/dt within this zone a sample of shredded burley tobacco was desiccated over calcium chloride. The DTG curve obtained was quite similar to that of the non-desiccated sample except for a marked decrease of over 60% in the dw/dt at 62°C and a 50% decrease in the weight loss from 25-150°C. When the desiccated sample was rehumidified, the derivative curve was qualitatively similar to that of the non-desiccated sample. It therefore appears that a considerable portion of the weight loss in this zone is due to the loss of adsorbed water.

Zone II (150-210°C). As shown by the derivative curves for the four tobacco types (**Figures 1, 2**), only the flue-cured and Turkish tobaccos exhibited a significant weight loss within this zone. The maximum dw/dt for both types exceeded 0.1 mg/°C. Although Maryland and burley tobaccos also exhibited some weight loss within this zone, both the per cent weight loss **Table 1** and the maximum rate of weight loss (**Figures 1, 2**) were considerably less than those for the flue-cured and Turkish tobacco. The blended tobaccos showed a similar weight loss in this zone. This was expected since the flue-cured and Turkish tobaccos comprised 60 percent of the blends (**Figure 3**).

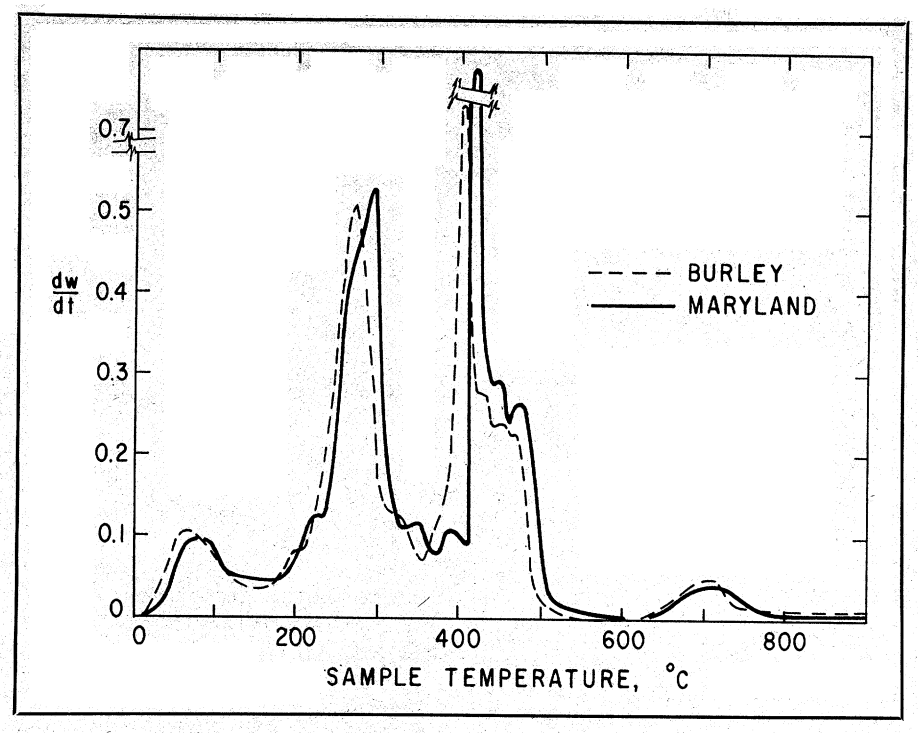

Fig. 1. Derivative thermograms of Maryland and burley tobaccos in air at 15°/min.

In an earlier report (8) the increasing weight losses for ground Maryland, burley, flue-cured and Turkish tobaccos over the temperature range of 135-150°C to 225-230°C were attributed to the degree of aromaticity of these tobaccos. Using differential thermal analysis, workers have attributed weight losses in this zone to the loss of hydrated water (2). Results obtained in this study are in agreement with these findings. Loss of weight in this zone is thought to be due primarily to volatilization and/or pyrolysis since no significant difference in weight loss occurred when the samples were run in both air and helium (**Table 1**).

Zone III (210-350°C). This is the first zone in which all of the tobacco types exhibited a considerable weight loss (**Table 1**). The derivative curves show significantly greater dw/dt maxima for the burley and Maryland tobaccos than for either the flue-cured or Turkish tobaccos (**Figures 1, 2**). This difference appears to be characteristic of the burley and Maryland tobaccos as compared to the flue-cured and Turkish tobaccos (8). For both the burley and Maryland to-

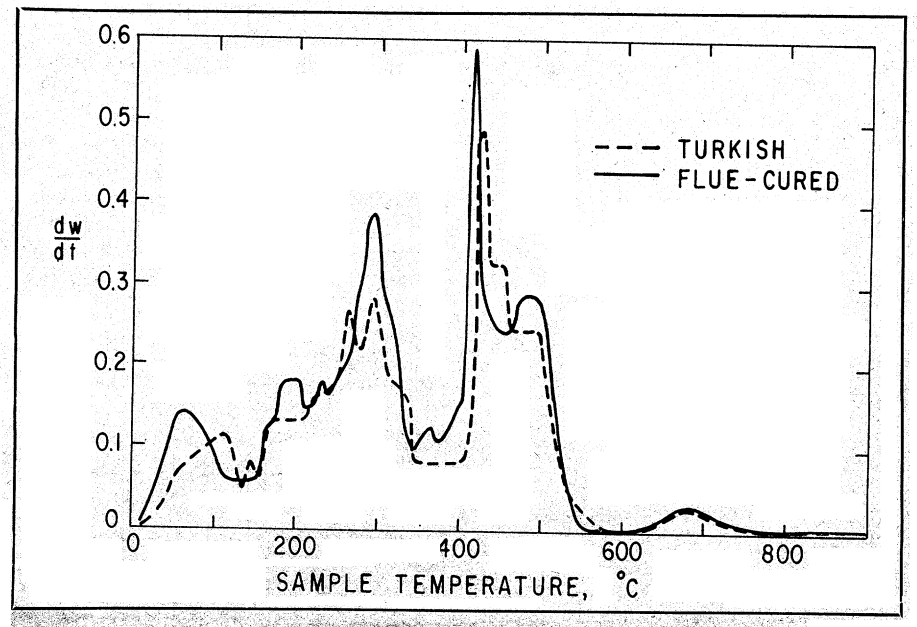

Fig. 2. Derivative thermograms of flue-cured and Turkish tobaccos in air at 15°/min.

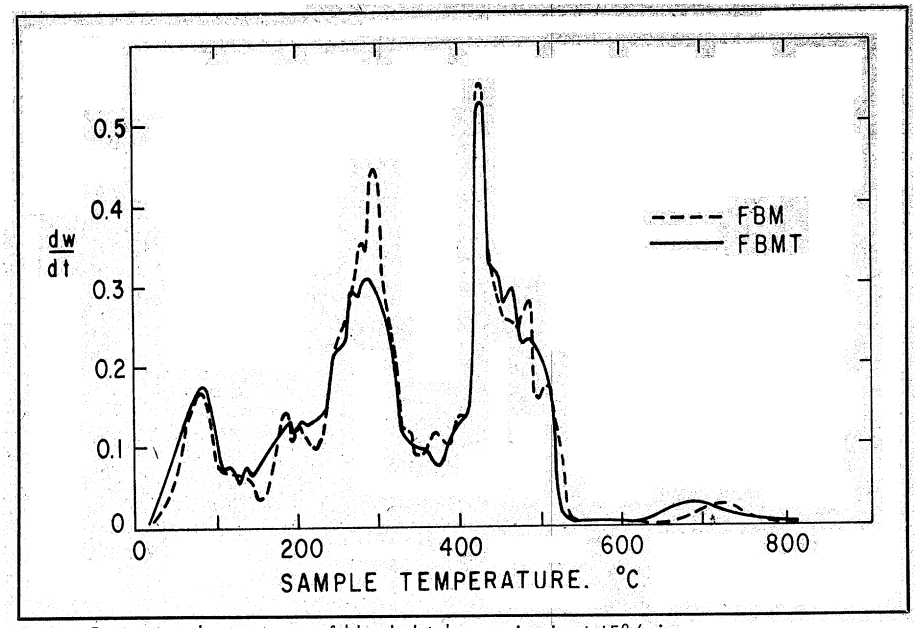

Fig. 3. Derivative thermograms of blended tobaccos in air at 15°/min.

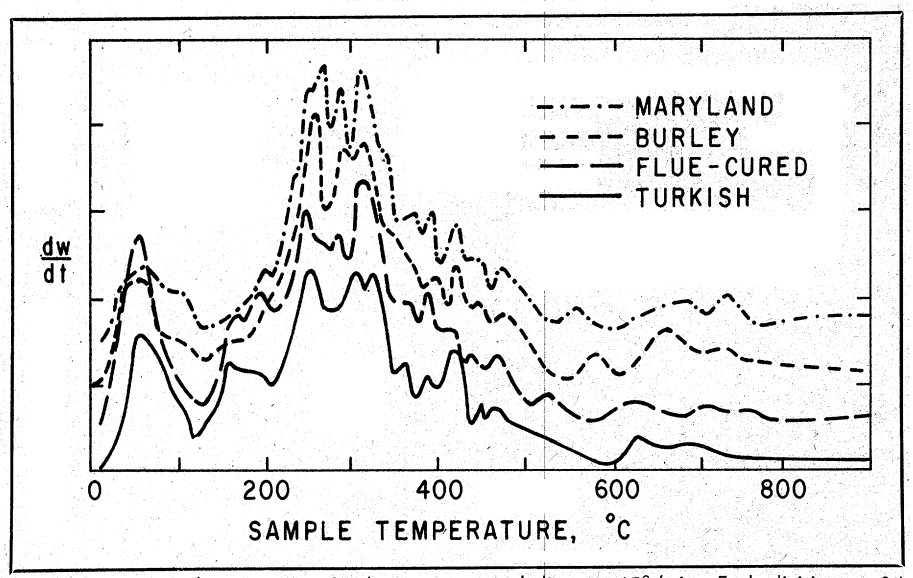

Fig. 4. Derivative thermograms of tobacco types in helium at 15°/min. Each division = 0.1 mg/°C.

Table 1. Percent weight loss for tobacco types and blends at a heating rate of 15°C per minute

Zone °C	I 25-150	II 150-210	III 210-350	IV 350-550	V 550-800	Total
			AIR			
Burley	9.5	3.5	33.5	30.0	3.5	79.0
Maryland	7.5	3.5	35.5	34.5	3.0	89.5
Turkish	8.5	7.0	27.5	35.0	2.5	80.0
Flue-cured	15.5	6.5	29.5	34.0	1.5	86.5
FBMT*	10.5	4.5	32.0	36.5	3.5	87.0
FBM**	12.5	5.5	29.0	35.0	2.0	84.0
			HELIUM			
Burley	10.5	2.0	27.0	18.5	7.5	66.5
Maryland	8.5	2.5	26.0	24.0	5.5	68.0
Turkish	12.0	5.0	26.0	16.5	4.5	64.5
Flue-cured	13.0	6.0	29.5	17.5	4.0	70.0
FBMT	9.0	4.0	28.5	16.5	4.5	62.5
FBM	9.5	4.0	27.5	17.5	7.0	65.5

Flue-cured, Burley, Maryland and Turkish Blend
Flue-cured, Burley and Maryland Blend

baccos there was a gradual increase in loss of weight from about 230-240°C to a maximum at temperatures of 275° and 295°C, respectively. After reaching these maxima, both types showed an almost constant rate of decrease to a minimum at 325-335°C. Loss of weight in this zone is probably due to volatilization of leaf constituents such as nicotine, pyrolysis of cellulose (2, 6) and lignin (6) and oxidative volatilization.

If only volatilization and pyrolysis occurred the use of air would have little effect on the weight loss. However, for the burley and Maryland tobaccos the total weight loss in air was 24-36 percent greater and the dw/dt maxima were about 60 percent greater than that in helium (**Table 1, Figures 1-4**). This indicates that for these tobaccos oxidative volatilization contributes significantly to the total weight loss. For the flue-cured and Turkish tobaccos no gross difference in weight loss occurred; and the dw/dt maxima were only about 30 percent greater when the samples were run in air compared with helium. Apparently, oxidative volatilization does not contribute as much to the weight loss for these two tobaccos as it does for the two air-cured types. For the blends, the somewhat greater weight losses which occur in air compared with helium appear to reflect the presence of burley and Maryland tobaccos (**Table 1**).

Zone IV (350-550°C). Loss of weight in this zone is due primarily to oxidation since the rapid weight loss which occurred when the samples were thermally decomposed in air did not occur in helium. The very rapid weight loss over the relatively narrow temperature range of 410-430°C for the four tobacco types indicates that self-supporting combustion occurred and was initiated at a minimum of 410°C (**Figures 1, 2**). This is in general agreement with an earlier report which stated that the ignition temperature of tobacco is between 442-488°C (9). Examination of the derivative curves for the four tobacco types showed that the maxima varied from 0.4 to 0.7 mg/°C. Weight losses for the burley and Maryland tobaccos were completed at a lower temperature than those for the flue-cured and Turkish tobaccos. It should be noted that pyrolytic reactions most likely occur in this zone and are probably enhanced by the exothermic oxidation reactions.

Zone V (550-800°C). Within this zone the dw/dt maxima have a rate of change less than 0.05 mg/°C and

account for only about 2-5% of the total weight loss. Even though this weight loss is small it could be important. Owing to the very high temperature and because similar weight losses occurred in both air and helium, the weight loss may be due primarily to pyrolytic reactions.

Thermal Decomposition in Helium—Heating Rate 15°C Per Minute

The primary purpose of using helium was to help identify those temperature zones in which either volatilization, pyrolysis or oxidation occurred. Thermal decomposition of the four tobacco types were similar (**Figure 4**). As in air the DTG curves were divided into five temperature zones: 25-150°, 150-210°, 210-350°, 350-550° and 550-800°C. Zones I, II and V were comparable to the same zones when the samples were run in air and have been discussed. Zone III (210-350°C) is the most characteristic region of pyrolysis. As indicated by the derivative curves obtained at a heating rate of 15°C/minute the weight loss is greatest in this zone (**Figure 4**). Three maxima are present. The order of decreasing dw/dt is Maryland > burley > flue-cured > Turkish. The DTG curve obtained when a heating rate of 3°C/minute was employed indicated that this order of dw/dt is independent of the heating rate. However, there are qualitative differences in the derivative curves which are dependent upon the heating rate. These will be discussed in another part of the paper. Comparison of the derivative curves of the four tobacco types in this zone showed that the Turkish tobacco is superficially different from the other tobacco types. This is perhaps due to the presence of the midrib which is not removed during processing of the Turkish leaf.

Examination of the derivative curves for both of the blended tobaccos indicates only superficial differences which possibly can be attributed to the presence or absence of Turkish tobacco. (**Figure 5**). There appears to be no major differences in the temperature of the maxima dw/dt for the blended tobaccos when compared with that of the different types (**Figures 4, 5**).

Loss of weight in Zone IV for the samples run in helium was approximately 50 percent below that in air (**Table 1**). The dw/dt maxima were decreased to an even greater extent Although loss of weight does occur in helium, the data obtained in air substantiate that the reactions occurring are primarily due to oxidation.

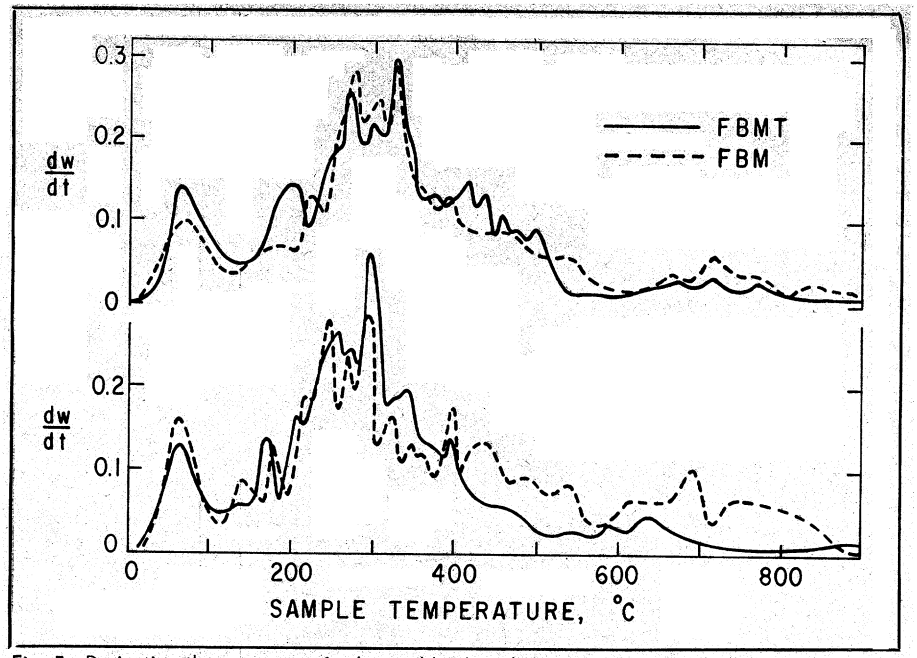

Fig. 5. Derivative thermograms of tobacco blends in helium at 3°/min. (bottom) and 15°/min. (top).

Heating Rate

The effect of the heating rate on thermal degradations has been reviewed (4, 5) and should be applicable to the thermal degradation of tobacco. The derivative curves for the types and blends of tobaccos heated at 3 and 15°C per minute for Zones I, II, III and V are generally

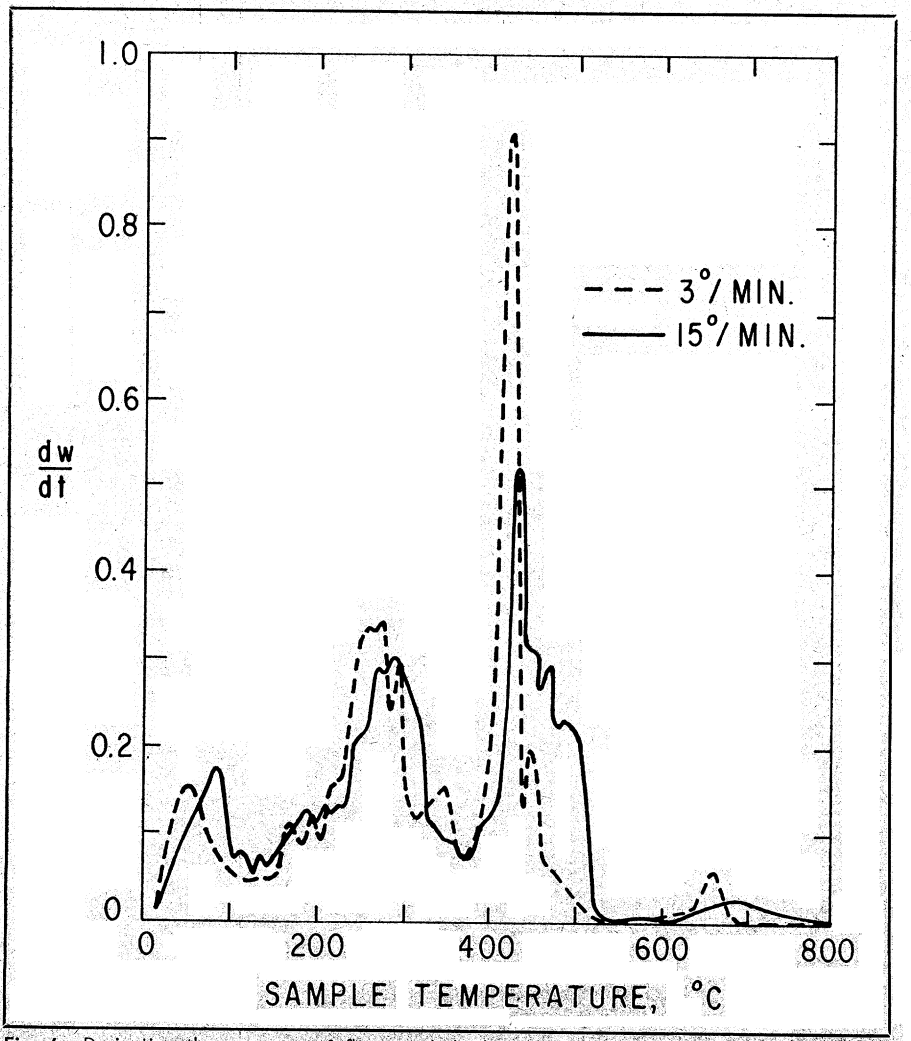

Fig. 6. Derivative thermograms of flue-cured, burley, Maryland and Turkish blends in air at different heating rates.

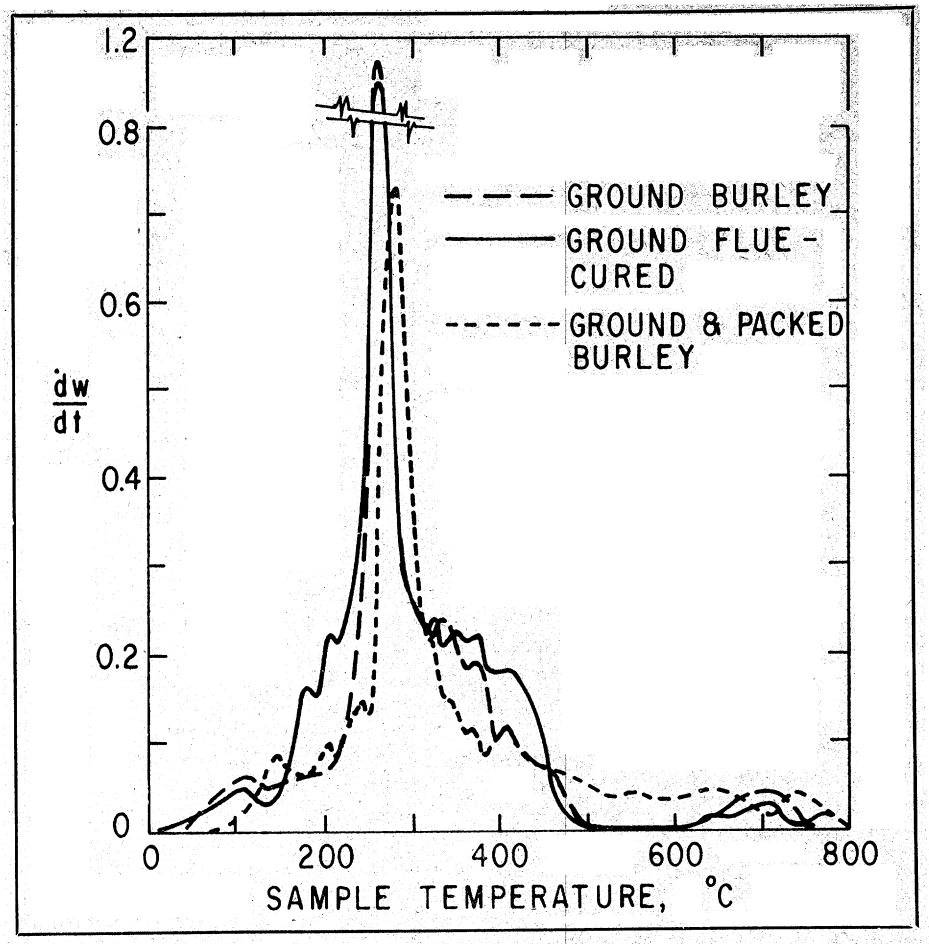

Fig. 7. Derivative thermograms for ground vs. ground and packed tobacco in air at 15°/min.

quite similar (**Figure 6**). At the lower heating rate the maxima of the DTG curves in these zones are 25-50°C lower than at the higher heating rate. This could be due to a smaller temperature difference within the sample. At the lower heating rate the sample temperature is more uniform, and there will be less overlap between specific pyrolytic or oxidative reactions than at the higher heating rate. There would also be better diffusion of the products formed at the lower heating rate which would allow more air to reach the sample (4). Also, there would be a smaller temperature difference between the sample and the sample thermocouple at the lower heating rate. This would result in a lower temperature at which the dw/dt maxima occurs.

The rate of heating had a marked effect on the derivative curve in Zone IV (**Figure 6**). In this zone, once the minimum temperature for ignition of the tobacco was attained, self-supporting oxidation took place. When this occurred dw/dt was no longer as dependent upon the heating rate but rather on the rate of oxidation of the ignited sample. This is evident since the weight loss in this zone began at almost the same temperature for both heating rates. The derivative curves show that at a heating rate of 3°C per minute the maximum rate of weight loss in Zone IV was considerably higher and reached a minimum at a lower temperature than at a heating rate of 15°C per minute. These differences may be due to a difference in the amount of air reaching the samples as a result of the different heating rates. For the higher heating rate, evolution of large quantities of gas from the sample may exclude air and result in a lower maximum rate of weight loss. When this takes place the rate of weight loss becomes dependent upon the amount of air reaching the sample. This results in a smaller rate of weight loss over a broader temperature range for the higher rate of heating (4). At both heating rates the decreasing order of dw/dt for the tobacco types in Zone IV was Maryland > burley > flue-cured > Turkish. This is in agreement with the observed burning rate of these tobaccos.

Ground and Packed Tobacco

To assess the effect of ground tobacco on its thermal decomposition, as compared with shredded tobacco, samples of ground burley and flue-cured tobaccos were thermally decomposed in air. The DTG curves obtained for both of these ground samples were similar (**Figure 7**). Unlike the DTG curves obtained for the shredded samples, which showed almost equal weight losses in both Zones III and IV, the curves for the ground samples showed the largest weight loss in Zone III. For the ground samples the dw/dt maximum (255°C) in Zone III was about three times greater, and in Zone IV was about two-thirds less, than that for the shredded samples. When the ground tobacco samples were packed in stainless steel holders, the derivative curves were similar to those of the unpacked ground samples (**Figure 10**). As was expected, the maximum dw/dt occurred at a temperature 15-25°C higher for the packed vs. the unpacked sample. The DTG curves for the ground and shredded burley samples run in helium indicated that the mode of thermal decomposition in the inert atmosphere is essentially independent of the physical state of the tobacco.

It is quite apparent that the ground tobacco samples are more reactive and undergo spontaneous ignition at a much lower temperature than the shredded samples. This is due to the finer particle size and increased surface area of the ground tobacco.

A previous report (8) mentioned that ground tobacco samples began to ignite at 225-230°C which is in agreement with data obtained in this study. It is recognized that ground tobacco is more homogeneous and is perhaps more useful in characterizing different tobacco types. However, for determining the effect of chemical modifiers on weight losses and dw/dt within defined temperature zones the use of shredded tobacco is thought to be more useful as it more closely approximates the physical state of the tobacco in the burning cigarette. Since the DTG curves for the shredded tobacco are more complex than the curves for ground tobacco, differences in the effect of various chemical modifiers have been easily recognized.

Summary

Some of the parameters effecting the thermogravimetric analysis of different types and blends of tobacco have been discussed. Shredded and ground samples were run in air and helium at heating rates of 3° and 15°C per minute. TGA curves were converted to their derivative

(DTG) curves. For comparison of the tobacco samples, these DTG curves were divided into five temperature zones. In Zone I (25-150°C) the maximum rate of weight loss in both air and helium occurred between 60-80°C and was shown to be due in large part to the volatilization of adsorbed water. In Zone II (150-210°C) the flue-cured and Turkish tobaccos exhibited the most significant weight loss. Loss of weight in this zone is thought to be due primarily to volatilization and/or pyrolysis. In Zone III (210-350°C) all tobacco types exhibited considerable weight loss; however, the burley and Maryland tobaccos exhibited significantly greater weight losses than the flue-cured and Turkish tobaccos. Loss of weight in this zone is probably due to volatilization, pyrolysis and oxidative volatilization. Weight loss occurring in Zone IV (350-550°C) is attributed primarily to oxidation since the rapid weight loss which occurred when the samples were thermally decomposed in air did not occur in helium. In this zone self-supporting oxidation is initiated at a temperature of approximately 410°C. Weight loss in Zone V (550-800°C) accounted for only about 2-5 percent of the total weight loss. As similar weight losses occurred in both air and helium pyrolysis is thought to be the predominant process taking place.

When the samples were run in helium loss of weight in Zones I, II and V were comparable to those of samples run in air. Zone III (210-350°C) was the most characteristic region of pyrolysis. Loss of weight in Zone IV was approximately 50 percent less than that in air, substantiating that the reactions occurring in this zone in air are in large part due to oxidation. The derivative curves for the types and blends of tobaccos heated at 3° and 15°C per minute for Zones I, II, III and V were quite similar. At the lower heating rate the maxima of the derivative curves in these zones were 25-50°C lower than at the higher heating rate. In Zone IV the rate of heating had a marked effect on the derivative curve. At a heating rate of 3°C per minute the maximum rate of weight loss was considerably higher and reached a minimum at a lower temperature than at a heating rate of 15°C per minute. The DTG curves for ground samples run in air showed the largest weight loss in Zone III. For these samples the maximum rate of weight loss in Zone III was about three times greater, and in Zone IV was about two-thirds less, than that for the shredded samples. As the derivative curves for ground and shredded burley samples run in helium were quite similar, the mode of thermal decomposition in the inert atmosphere is thought to be essentially independent of the physical state of the tobacco.

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